

THE EFFECTS OF IMPACT ON D/H OF HORNBLENDES: APPLICATIONS TO SNC PETROGENESIS.

M.E. Minitti, M.J. Rutherford, B.J. Giletti and P.H. Schultz, Department of Geological Sciences, Brown University, Box 1846, Providence RI 02912, e-mail Michelle_Minitti@brown.edu.

Abstract. The long-standing question of the Martian water budget has been addressed by studies of hydrous minerals contained within the SNC meteorites, widely believed to be of Martian origin. These minerals are characterized by low H contents and elevated D relative to terrestrial materials [1]. An explanation for these observations is the preferential loss of ^1H due to non-equilibrium fractionation of ^1H relative to D during impact. Impact experiments were conducted on amphibolite and ion microprobe analyses of shocked and unshocked hornblende were carried out to test impact as a mechanism of relative D-enrichment. Shocked hornblende was found to have D/H ratios 2-4 times greater than those of unshocked hornblende.

Introduction. The dry surface of present-day Mars contrasts with surface features created in its past by flowing water. Due to its weak gravitational field, Mars is believed to have lost most of its water through the gradual escape of volatiles from the upper atmosphere. Water also may reside in a reservoir of ground ice [2]. Ideally, knowledge of crustal and mantle water contents would place constraints on the amount of water Mars had originally and how much has been lost through atmospheric escape.

The SNC (Shergotty-Nakhla-Chassigny) meteorites, which are generally accepted to be of Martian origin, allow indirect analyses of the water budget of Mars. Three of the SNC meteorites have melt inclusions containing hydrous minerals. Floran et al. [3] first discovered kaersutitic amphiboles within a Chassigny melt inclusion. A later study [4] also found kaersutite within Zagami and Shergotty melt inclusions. Biotite was found within a Chassigny melt inclusion [5] and OH-bearing apatite is present within Zagami but not within a melt inclusion [6].

These hydrous minerals have been studied in order to address the question of water on Mars. Johnson et al. [5] experimentally and theoretically studied the kaersutites, biotite and melt inclusions of the Chassigny meteorite. The theoretical portion of the study involved back calculating the original composition of the melt trapped within the inclusion. Beginning with the glass composition of the inclusion and using findings from [3] regarding OH contents of the Chassigny kaersutite, they calculated how much water had to be present in the original melt inclusion to stabilize kaersutite. Employing the weight percent of water necessary for kaersutite crystallization and the percent of crystallization that had occurred within the melt inclusion prior to kaersutite formation, they arrived at a melt water content of 1.4 wt%. Similar studies of melt inclusion kaersutites in other meteorites yielded comparable water contents [7].

A more recent study by Watson et al. [1] measured the H content of all the hydrous minerals using an ion

microprobe and found H levels averaging ten times lower than those suggested by [5] and [7]. Watson et al. [1] also used an ion microprobe to measure the deuterium (D) to hydrogen (H) ratios of the hydrous minerals. They found D values (+512‰ to +4358‰) high, though generally less than the D value of the Martian atmosphere (+4000‰). D measurements also revealed D variations from grain to grain of up to 900‰ and within single grains of up to 1000‰. The elevated and variable values were explained as the result of extensive but incomplete exchange between the minerals and the atmosphere and hydrosphere. According to [1], the exchange occurred by diffusion through the host olivine and pyroxene phenocrysts and through the melt inclusion glass.

The interpretation of the high and variable values by [1] poses intriguing difficulties. The variable D throughout the melt inclusion phases requires low temperatures to prevent the diffusion of D and ^1H and homogenization of D/H. Such temperatures along with the exchange of D and ^1H through the olivine and pyroxene hosts would be expected to produce alteration of the olivine and pyroxene. Low temperature alteration of neither mineral is observed. Perhaps the most difficult observation to explain using the interpretation in [1] is the absence of D or ^1H within the glasses surrounding the melt inclusion crystals. Both [5] and [1] found the melt inclusion glass to be anhydrous.

An alternative explanation for the low H contents and high D of the hydrous minerals is the preferential loss of ^1H during impact shock due to non-equilibrium fractionation of H. Examples exist in both the chemical and geologic literature of non-equilibrium fractionation of H. Electrolysis of water concentrates D in the liquid phase with a fractionation factor of up to 10 [8]. Impact-induced devolatilization experiments on serpentine yielded D-enriched (D = 19‰) solid residue [9]. In the present study, impact experiments and ion microprobe analyses were carried out to test the impact fractionation explanation for the low H contents and high and variable D of the SNC hydrous minerals.

Experimental. Impact experiments were conducted on garnet-poor Gore Mountain, NY amphibolite [10]. Thin sections of the amphibolite show subhedral grains of hornblende and plagioclase with minor orthopyroxene and rare biotite. This sample serves as a reasonable analog for the SNC phases of interest and contains an equal abundance of hornblende and plagioclase. The presence of plagioclase is important because conversion of plagioclase to maskelynite is one indication of shock pressure common to many SNC meteorites. A 3.8 cm x 3.8 cm x 2.5 cm block of the Gore Mountain amphibolite was impacted in the NASA Ames Vertical Gun Range. The impact chamber was evacuated to a pressure of 0.5 torr. A stainless steel projectile (0.1319 g, 0.3175 cm diameter)

IMPACT EFFECTS ON D/H OF HORNBLENDES: M.E. Minitti et al.

was fired in a vertical impact at a velocity of 4.97 km/s into the block. The peak shock pressure of the experiment was estimated at 70 GPa based on theoretical calculations of peak shock pressure done for an iron projectile into a gabbroic anorthosite at 5 km/s, which should be comparable to the conditions here [11]. The impact produced a collection of single grain fragments and still-intact aggregates of grains. The impacted material was not kept under vacuum during its transfer from Ames or during its storage at Brown.

Analytical. Individual grains and aggregates that demonstrated shock effects were hand-picked for analysis. The criteria for selection of highly shocked hornblende were a powdery appearance and ready friability. Aggregates were judged to be highly shocked when they contained powdery white plagioclase. Hornblende was also chosen with care in order to avoid grains of orthopyroxene and grains of biotite associated with the hornblende. Thin sections of the shocked material reveal fractured hornblende and plagioclase and plagioclase with undulose extinction. Thin sections were made of a portion of all shocked plagioclase fragments. In these thin sections, no maskelynite was found replacing plagioclase. The presence of maskelynite would additionally constrain the shock pressures experienced by the material to be above 30-35 GPa (12).

Polished ion microprobe mounts were made containing impacted and non-impacted individual grains and aggregates. Before analysis, the mounts were held under a vacuum of 1×10^{-6} torr for 16-24 hours. They were immediately gold coated upon removal and then were transferred to an ampoule which was kept under a vacuum of 0.05 torr by a rotary pump. The ampoule was used to transport the mounts to the ion microprobe. The collective time the samples spent outside of a vacuum during the transfer steps was no more than ten minutes.

Isotopic measurements were made of ^1H , D, ^{30}Si and ^{43}Ca on the Cameca IMS 3f ion microprobe at the Woods Hole Oceanographic Institution Regional Facility. The primary beam was chosen in the range of 100-200 nA, and a field aperture of either 68 μm or 150 μm was utilized. Various voltage offsets were used ranging from 0 to -40 V (energy filtering). The area rastered was relatively small with an axial beam size of 30 μm . The primary beam diameter itself ranged between 60-120 μm . Because of the low count rate for D (3-5 counts/s), long count times and from 15 to 45 measuring cycles were used to obtain enough counts to bring the ± 2 uncertainty level in the measurements to within 8%.

Results. D/H, $\text{H}/^{30}\text{Si}$ and $^{43}\text{Ca}/^{30}\text{Si}$ ratios were calculated from the analyses of both impacted and non-impacted samples. The shocked samples displayed elevat-

-ed D/H ratios and depressed $\text{H}/^{30}\text{Si}$ ratios relative to the unshocked samples. The D/H ratios of the shocked samples were 2-4 times greater than those of the unshocked samples. Smaller magnitude changes in $\text{H}/^{30}\text{Si}$ ratios were observed with shocked $\text{H}/^{30}\text{Si}$ ratios 2-2.5 times less than unshocked $\text{H}/^{30}\text{Si}$ ratios. The $^{43}\text{Ca}/^{30}\text{Si}$ ratios of the shocked and unshocked hornblendes were the same to within 10%.

Discussion. These results suggest that the impact produces D/H in hornblende that is 2-4 times that in unshocked hornblende. Release of some of the mineral H with a very low D/H yields the elevated D/H of the shocked hornblende. The difference in the magnitude of the variations in D/H and $\text{H}/^{30}\text{Si}$ ratios might be explained by the post-impact adsorption of water vapor with D/H less than the D/H of the hornblende. Adsorbed water would lower the D enrichment of shocked hornblende thereby decreasing its D/H. Adsorbed water would also increase the measured $\text{H}/^{30}\text{Si}$ ratios. If subsequent adsorption by the shocked hornblende occurred, the observed degree of enrichment measured as an impact effect is a minimum.

These experiments imply that all the SNC meteorites, which have come to Earth via impact processes, contain an inherent bias toward high D/H ratios in their amphiboles. Conclusions regarding the Martian water budget drawn from these D and ^1H compositional data are in turn affected. It is also likely that the D/H ratios of other OH-bearing minerals, such as the biotite and apatite found in Chassigny [5] and Zagami [6] are similarly affected by involvement in impact. Consideration must be given to the effect of shock on D and ^1H contents in order to assess the question of water on Mars accurately.

References: [1] Watson L.L., Hutcheon I.D., Epstein S. and Stolper E.M. (1994), *Science*, 265, 86-90. [2] Carr M. and Wänke H. (1991) *LPSC XXII*, 181-182. [3] Floran R.J., Prinz M., Hlava P.F., Keil K., Nehru C.E. and Hinthorne J.R. (1978), *Geochim. Cosmochim. Acta*, 42, 1213-1229. [4] Treiman A.H. (1985), *Meteoritics*, 80, 229-243. [5] Johnson M.C., Rutherford M.J. and Hess P.C. (1991) *Geochim. Cosmochim. Acta*, 55, 349-366. [6] Vistisen L., Petersen D. and Madsen M.B. (1992), *Phys. Scr.*, 46, 94. [7] McSween H.Y., Jr. and Harvey R.P. (1993), *Science*, 259, 1890-1892. [8] Kirshenbaum I., Urey H.C. and Murphy G.M. (1951) *Physical Properties and Analysis of Heavy Water*. New York: McGraw-Hill Book Company, Inc. 188-191. [9] Tyburczy J.A., Krishnamurthy R.V., Epstein S. and Ahrens T.J. (1990) *EPSL*, 98, 245-260. [10] Wentorf R.H., Jr. (1956) *Am. Jnl. Sci.*, 254, 413-419. [11] Orphal et al. (1980) *Proc. Lunar. Planet. Sci. Conf.*, 11, 2309-2323. [12] Stöffler D., Keil K. and Scott E.R.D. (1991) *Geochim. Cosmochim. Acta.*, 55, 3845-3867.